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(71) Applicant: **Chung Pak Battery Works Ltd., Kowloon, Hong Kong (CN)**

(72) Inventor: **YE, Jinhua**
7/F, Chung Pak Commercial Bldg.
Kowloon
Hong Kong (CN)

(74) Representative: **Kramer - Barske - Schmidtchen**
Radeckestrasse 43
81245 München (DE)

(54) NEGATIVE ELECTRODE OF DRY BATTERY, MANUFACTURE METHOD OF THE SAME, AND ZINC-MANGANESE DRY BATTERY USING THE SAME

(57) The present invention relates to dry cells, it discloses a negative electrode body for dry cells, comprising (by weight): 0.0005~0.010% magnesium; 0.001~0.005% indium or 0.0005~0.005% tin; 0~0.004% lead; 0~0.0005% cadmium; the rest being zinc. It also discloses the preparing method of said negative electrode body for dry cells. It further discloses a Zn/MnO_2 dry cell, including said negative electrode body of the present invention, on the inner surface of which places a coated paper, the outer of which are PVC sheath and iron shell. Inside the coated paper there are powdery bobbin and carbon rod, there is bobbin washer over the powdery bobbin, on the bottom side of the Zn/MnO_2 dry cell there are bottom cap and bottom seal, and on the upper side of it there are rubber plug, top cap and upper seal. It is necessary to add lead and cadmium for the preparation of the prior art zinc can used for the negative electrode body of Zn/MnO_2 dry cell, whereas metal indium or tin is added in place of lead and cadmium for the preparation of the zinc can of the present invention. Compared with prior arts, an advantage of the Zn/MnO_2 dry cells of the present invention is that they are free of lead and cadmium, the preparing process without the addition of lead and cadmium does not lead to environmental pollution, and meets the requirements of environmental protection.

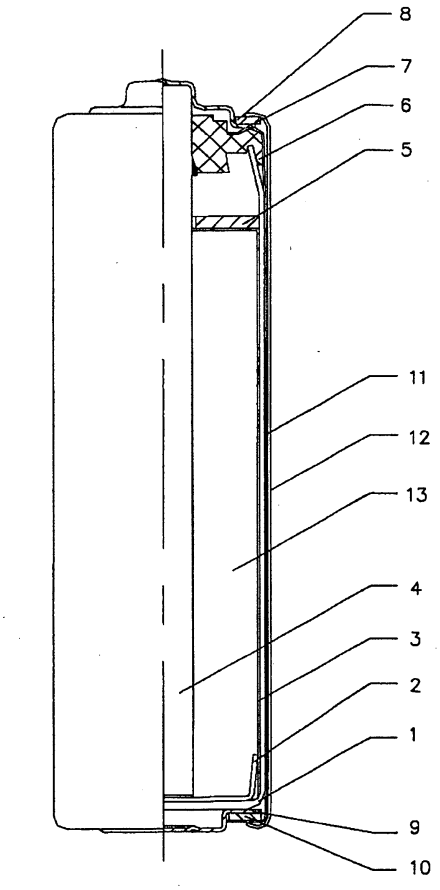

FIG. 1

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to dry cells, particularly to a negative electrode body for Zn/MnO_2 dry cells, its preparing method, and Zn/MnO_2 dry cells using it thereof.

BACKGROUND OF THE INVENTION

[0002] The negative electrode body of the commonly used Zn/MnO_2 dry cell is a zinc can. In order to improve the ductility and strength of zinc metal, it is necessary to add 0.3-0.5% lead (Pb), 0.001-0.004% cadmium (Cd) and 0.0005-0.0030% magnesium (Mg) during zinc casting. Lead and cadmium are heavy metals, their uses being restricted by international environmental protection organizations, so, it is necessary to obtain Zn/MnO_2 dry cells, which are free of lead and cadmium for the purpose of environmental protection.

SUMMARY OF THE INVENTION

[0003] This invention provides a negative electrode body of dry cells, which is fabricated without the addition of lead and cadmium.

[0004] This invention also provides a method for preparing said negative electrode body of dry cells.

[0005] Another object of this invention is to provide a Zn/MnO_2 dry cell using said negative electrode body.

[0006] To achieve the object of the present invention, the negative electrode body of dry cells comprises (by weight):

0.0005~0.010% magnesium;
0.001~0.005% indium or 0.0005~0.005% tin;
0~0.004% lead;
0~0.0005% cadmium;
the rest being zinc.

[0007] Another object of this invention can thus be achieved: the method for preparing said negative electrode body of dry cells comprises: zinc ingots of which zinc content is above 99.9955%, cadmium content≦ 0.0005% and lead content≦ 0.004% are used, and 0.0005~0.010% magnesium, 0.001~0.005% indium or 0.0005~0.005% tin are added; it is cast into zinc plate under casting temperature of 400°C~500°C, rolled, and punched into zinc particles with punch press, the punched zinc particles are given surface deburring and lubricant treatments, then the obtained zinc particles are punched into zinc can by a high-speed precision extruder.

[0008] Still another object of this invention can thus be achieved: the Zn/MnO_2 dry cell includes said negative electrode body of the present invention, the inner surface of which lies a coated paper, the outer of which are PVC sheath and iron shell, inside the coated paper are powdery bobbin and carbon rod, with the bobbin washer over the powdery bobbin. On the bottom side of the Zn/MnO_2 dry cell there are bottom cap and bottom seal, and on the upper side of it there are rubber plug, top cap and upper seal.

[0009] The zinc cans of the negative electrode bodies of the prior art Zn/MnO_2 dry cells contain lead and cadmium, whereas metal indium or tin is added in place of lead and cadmium to the zinc cans of the present invention. Compared with prior arts, an advantage of the Zn/MnO_2 dry cells of the present invention is that they are free of lead and cadmium. The preparing process without the addition of lead and cadmium does not lead to environmental pollution, and meets the requirements of environmental protection.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The negative electrode body of the present invention comprises (by weight):

0.0005~0.010% magnesium;
0.001~0.005% indium or 0.0005~0.005% tin;
0~0.004% lead;
0~0.0005% cadmium;
the rest being zinc.

[0011] Referring to Fig. 1, the Zn/MnO_2 dry cell includes the negative electrode body of the present invention, (i.e. the zinc can 1), on the inner surface of which places a coated paper 3, the outer of which are polyvinyl chloride (PVC) sheath

11 and iron shell 12. Inside the coated paper 3 are powdery bobbin 13 and carbon rod 4, there is a paper cup 2 under the powdery bobbin 13 and carbon rod 4. There is bobbin washer 5 over the powdery bobbin 13. On the bottom side of the Zn/MnO_2 dry cell there are bottom cap 9 and bottom seal 10, and on the upper side of it there are rubber plug 6, top cap 7and upper seal 8.

[0012] The negative electrode body of the dry cell, i.e. the zinc can, can be prepared by conventional process.

[0013] At first, zinc particles are prepared. Zinc ingots of which zinc content is above 99.9955%(cadmium content≦ 0.0005% and lead content≦ 0.004%) are used; and 0.0005~0.010% magnesium, 0.001~0.005% indium or 0.0005~0.005% tin are added instead of lead and cadmium; it is cast into zinc plate under casting temperature of 400°C~500°C and rolled, then punched into zinc particles with required shape and size by punch press. It is necessary for the punched zinc particles to be given surface deburring and lubricant treatments.

[0014] By a high-speed precision extruder, the obtained zinc particles are punched into zinc can 1, then it is put on the production line, joined with coated paper 3, paper cup 2 and powdery bobbin 13. The bobbin washer 5 is put over the powdery bobbin, carbon rod 4 is inserted and rubber plug 6 is set, then polyvinyl chloride sheath 11 is enwrapped, the upper and bottom cap 7, 9 and bottom seal 10 are added, then the colored iron shell 12 and upper seal 8 are enwrapped, finally the dry cell is obtained after sealing.

EMBODIMENT 1

[0015] The negative electrode body of the present invention comprises (by weight):

0.0015% magnesium;
0.001 % indium;
0.0018% lead;
0.0002% cadmium;
the rest being zinc.

[0016] The Zn/MnO_2 dry cell of this embodiment includes the negative electrode body of the present invention, i.e. the zinc can 1, on the inner surface of which places a coated paper 3, the outer of which are polyvinyl chloride (PVC) sheath 11 and iron shell 12. Inside the coated paper 3 are powdery bobbin 13 and carbon rod 4, and there is a paper cup 2 under the powdery bobbin 13 and carbon rod 4. There is bobbin washer 5 over the powdery bobbin 13. On the bottom side of the Zn/MnO_2 dry cell there are bottom cap 9 and bottom seal 10, and on the upper side of it there are rubber plug 6, top cap 7 and upper seal 8.

[0017] The negative electrode body of the dry cell, i.e. the zinc can 1, can be prepared by conventional process.

[0018] While casting the metal zinc for negative electrode body , 0.0015% magnesium and 0.001% indium are added instead of lead and cadmium; it is cast into zinc plate under melting temperature of 400°C~500°C and rolled, then punched into zinc particles with required shape and size by punch press. It is necessary for the punched zinc particles to be given surface deburring and lubricant treatments; the obtained zinc particles are punched into zinc can 1 by a high-speed precision extruder.

[0019] The zinc can 1 is put on the production line; joined with coated paper 3, paper cup 2 and powdery bobbin 13. The bobbin washer 5 is put over the powdery bobbin, carbon rod 4 is inserted and rubber plug 6 is set, then polyvinyl chloride sheath 11 is enwrapped, the upper and bottom cap 7, 9 and bottom seal 10 are added, then the colored iron shell 12 and upper seal 8 are enwrapped, thus the dry cell is obtained after sealing.

EMBODIMENT 2

[0020] This embodiment is essentially the same as embodiment 1, except that the indium content of said composition is 0.002%, thus a Zn/MnO_2 dry cell with a negative electrode body of zinc can containing magnesium and 0.002% indium is obtained.

EMBODIMENT 3

[0021] This embodiment is essentially the same as embodiment 1, except that the indium content of said composition is 0.005%, thus a Zn/MnO_2 dry cell with a negative electrode body of zinc can containing magnesium and 0.005% indium is obtained.

EMBODIMENT 4

[0022] This embodiment is essentially the same as embodiment 1, except that 0.005% tin is used instead of said

indium, thus a Zn/MnO_2 dry cell with a negative electrode body of zinc can containing magnesium and 0.005% tin is obtained.

EMBODIMENT 5

[0023] This embodiment is essentially the same as embodiment 4, except that the tin content is 0.002%, thus a Zn/MnO_2 dry cell with a negative electrode body of zinc can containing magnesium and 0.002% tin is obtained.

EMBODIMENT 6

[0024] This embodiment is essentially the same as embodiment 4, except that the tin content is 0.005%, thus a Zn/MnO_2 dry cell with a negative electrode body of zinc can containing magnesium and 0.005% tin is obtained.

[0025] The obtained zinc particles of embodiments 1 to 6 are tested with Atomic Absorption Spectrometer (AAS), and the results are listed below:

Example	Amounts of addition (%)					Analyzed results of zinc particles (%)		Analyzed results of the cells (%)	
	Lead (%)	Cadmium (%)	Magnesium (%)	Indium (%)	Tin (%)	Lead (%)	Cadmium (%)	Lead (%)	Cadmiu m (%)
embodiment 1	0	0	0.0015	0.001	0	0.0018	0.0002	0.0004	0.00006
embodiment 2	0	0	0.0015	0.002	0	0.0018	0.0002	0.0004	0.00006
embodiment 3	0	0	0.0015	0.005	0	0.0018	0.0002	0.0004	0.00006
embodiment 4	0	0	0.0015	0	0.0005	0.0018	0.0002	0.0004	0.00006
embodiment 5	0	0	0.0015	0	0.002	0.0018	0.0002	0.0004	0.00006
embodiment 6	0	0	0.0015	0	0.005	0.0018	0.0002	0.0004	0.00006
Comparative example (presently used)	0.4	0.0005	0.0015	0	0	0.45	0.0006	0.071	0.00008
Note: 98/101/EEC specification: Lead<0.4%, cadmium <0.025%									

[0026] The surfaces of the zinc cans punched from zinc particles of embodiments 1 to 6 are equivalent to that of the Zn/MnO_2 dry cells now available (with the addition of 0.3-0.5% lead, 0.0005-0.004% cadmium).

[0027] The shelf performances of the R6 Zn/MnO_2 primary cells fabricated with the zinc plates obtained from embodiments 1 to 6 and the cells shelved at 60 °C and 90 % RH for 10 days are compared with the performance of the cell presently used (The negative electrode containing 0.3-0.5 % lead and 0.0005-0.004 % cadmium). (Evaluated at 20 °C):

Example	Comparison of the shelf performances of the cells			
	Primary cells (within 15 days)		Cells shelved at 60 °C and 90 % RH for 10 days	
	Open-circuit Voltage (V)	5 Ω Load Voltage (V)	Open-circuit Voltage (V)	5 Ω Load Voltage (V)
embodiment 1	1.70	1.55	1.59	1.46
embodiment2	1.70	1.55	1.60	1.48
embodiment 3	1.70	1.55	1.59	1.47
embodiment4	1.70	1.55	1.59	1.46
embodiment5	1.70	1.55	1.60	1.47
embodiment 6	1.70	1.55	1.59	1.47
Comparative Example (Presently used)	1.70	1.55	1.61	1.47

[0028] From said embodiments and results, it can be seen that the results of embodiments 2, 3, 4 and 5 are better.

[0029] From above results, it can be seen that both the contents of lead and cadmium of the Zn/MnO_2 dry cells of the present invention are within the maximum allowable level of 98/101/EEC specifications. Lead content is under 0.004%, and cadmium content is under 0.0005%, both satisfying the requirement of environmental protection, and can be used as Pb-free and Cd-free Zn/MnO_2 battery.

[0030] Although the present invention has been fully described by way of examples, it is noted that the descriptions are not limitations of the invention, various changes of the examples with reference to the descriptions will be apparent to those skilled in the art, and they should be considered as being included within the scope and spirit of the appended claims.

Claims

1. A negative electrode body for dry cells comprising (by weight):

0.0005~0.010% magnesium;
0.001~0.005% indium or 0.0005~0.005% tin;
0~0.004% lead;
0~0.0005% cadmium;
the rest being zinc.

2. The negative electrode body for dry cells according to claim 1, wherein the negative electrode body comprises (by weight):

0.0015 % magnesium;
0.001% indium;
0.0018% lead;
0.0002% cadmium;
the rest being zinc.

3. The negative electrode body for dry cells according to claim 1, wherein the negative electrode body comprises (by weight):

0.0015% magnesium;
0.002 % indium;
0.0018% lead;
0.0002% cadmium;
the rest being zinc.

4. The negative electrode body for dry cells according to claim 1, wherein the negative electrode body comprises (by weight):

0.0015% magnesium;
0.005% indium;
0.0018% lead;
0.0002% cadmium;
the rest being zinc.

5. The negative electrode body for dry cells according to claim 1, wherein the negative electrode body comprises (by weight):

0.0015 % magnesium;
0.0005% tin;
0.0018% lead;
0.0002% cadmium;
the rest being zinc.

6. The negative electrode body for dry cells according to claim 1, wherein the negative electrode body comprises (by

weight):

0.0015 % magnesium;
0.002% tin;
0.0018% lead;
0.0002% cadmium;
the rest being zinc.

7. The negative electrode body for dry cells according to claim 1, wherein the negative electrode body comprises (by weight):

0.0015 % magnesium;
0.005% tin;
0.0018% lead;
0.0002% cadmium;
the rest being zinc.

8. A method of preparing the negative electrode body for dry cells of claim 1, comprising: using zinc ingots of which zinc content is above 99.9955%, cadmium content ≦ 0.0005% and lead content ≦ 0.004%, adding 0.0005~0.010% magnesium and 0.001~0.005% indium or 0.0005~0.005% tin; casting into zinc plate under casting temperature of 400°C~500°C, rolling, punching into zinc particles with punch press, giving the punched zinc particles surface deburring and lubricant treatments, then punching the obtained zinc particles into zinc can by a high-speed precision extruder.

9. A Zn/MnO_2 dry cell, including any one of said negative electrode body of claims 1 to 7, on the inner surface of which places coated paper, the outer of which are PVC sheath and iron shell, inside the coated paper being powdery bobbin and carbon rod, the bobbin washer being over the powdery bobbin, on the bottom side of the Zn/MnO_2 dry cell there being bottom cap and bottom seal, on the upper side of it there being rubber plug, top cap and upper seal.

10. The Zn/MnO_2 dry cell according to claim 9, wherein there is paper cup under said powdery bobbin and carbon rod.

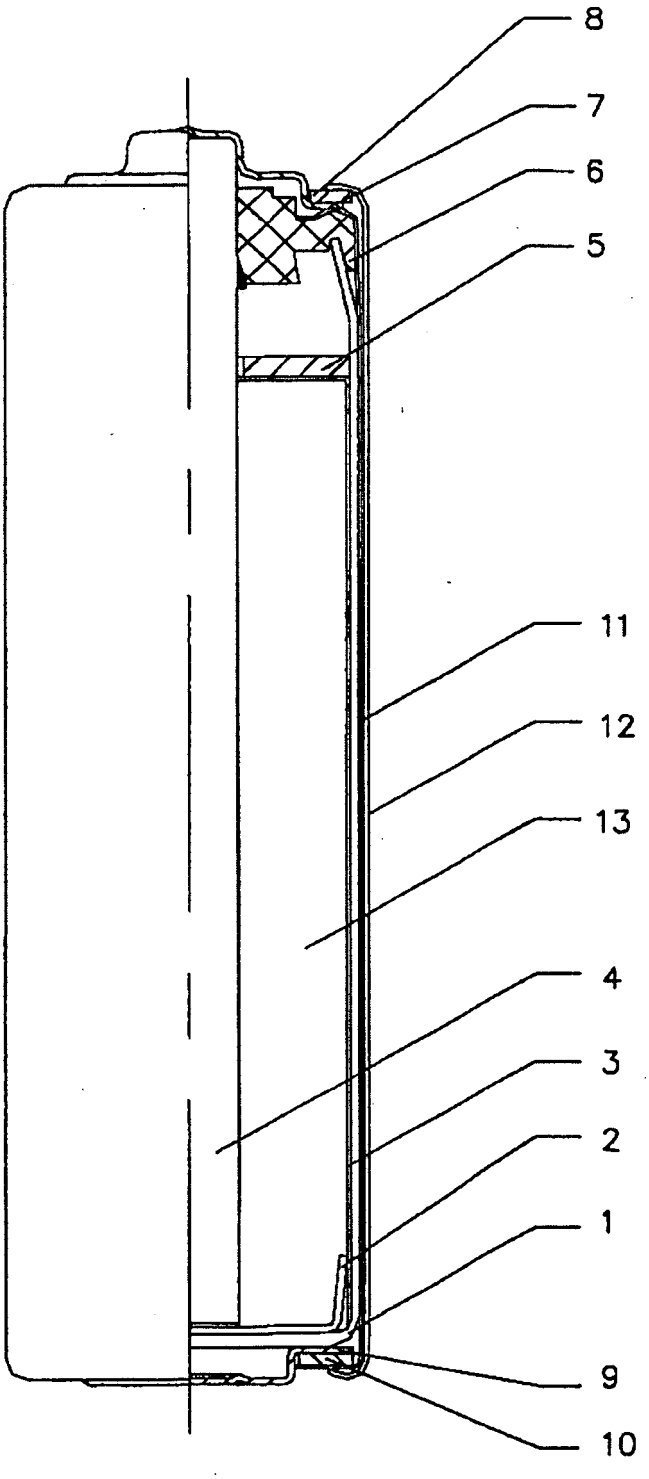

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2004/001556

A. CLASSIFICATION OF SUBJECT MATTER

IPC[7] H01M 4/42, 6/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[7] H01M 4/42, 4/38, 4/36, 6/06, 6/08, 6/10, 6/12, 6/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

CNPAT

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, PAJ, EPODOC: dry battery cell neagtive electrode anode zinc manganese magnesium indium tin Zn Mn Mg In Sn CNPAT: 锌 锰 干电池 镁 铟 锡 Mg In Sn Zn Mn

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP2003-317713A, 07 November 2003 (07. 11.2003), see claim 1.	1,8—10
A		2—7
X	JP2003—317715A, 07 November 2003 (07. 11.2003), see claim 1.	1,8—10
A		2—7
A	JP2001—185136A, 06. July 2001 (06.07.2001), see the whole document.	1—10
A	JP2001—229923A, 24 August 2001 (24.08.2001), see the whole document.	1—10

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23. February 2005(23.02.2005)	10 · MAR 2005 (10 · 03 · 2005)
Name and mailing address of the ISA/ 6 Xitucheng Road, Jimen Bridge, Haidian District, Beijing, 100088, P.R.China Facsimile No. 86-10-62019451	Authorized officer TIAN, Hong Telephone No. 86-10-62085037

Form PCT/ISA /210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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